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Ab initio computational study of the electronic and magnetic properties of the HoNi*Z* compounds accounting for electronic correlations

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Abstract. In this paper, the electronic structure and magnetic properties of the ternary intermetallics of the HoNi*Z* series (*Z* = Ga, Si, Al) is studied using the LSDA+*U* first-principles method. An analysis of the densities of electronic states in the compounds HoNiGa, HoNiSi, and HoNiAl with accounting for electronic correlations is performed.

1. Introduction

The series of ternary intermetallic compounds *RTX*, with *R* standing for a rare-earth element, *T* is a transition metal element, and *X* is a p-block element, represents a vast area of interesting magnetic compounds in the family of rare-earth based intermetallics. Many of its members show remarkable magnetic and electrical properties in a wide range of temperatures [1]. It has been observed that some *RTX* compounds show a large magnetocaloric effect (MCE) [2-4] and magnetoresistance (MR) close to their ordering temperatures [5]. The large MCE in these compounds is due to large magnetic moments and large changes in magnetization at different temperatures. The field induced metamagnetic transition in some of these compounds also results in large MCE and MR. It is well known that the both MCE and MR results from the interplay of magnetic sub-lattices within the magnetic field and therefore, these two properties are also revealed simultaneously. In fact, such a correlation was observed in many materials [6-8].

In *R*NiSi belonging to the *RTX* series, the compounds with *R* = La-Nd crystallize in LaPtSi type tetragonal structure. LaNiSi is found to show superconductivity with a critical temperature T_C of 1.2 K [4]. CeNiSi shows Kondo behavior, whereas in NdNiSi two antiferromagnetic transitions were found at the Neel temperatures T_{N1} = 6.8 K and T_{N2} = 2.8 K [6]. The authors also reported the effects of hydrogenation of these compounds and observed that on insertion of hydrogen, the Kondo effect in CeNiSi strengthens. On the other hand, the antiferromagnetic transitions in NdNiSi disappear and no magnetic ordering is found in hydrogenated NdNiSi down to 2 K [6]. HoNiSi and ErNiSi show collinear magnetic structure at 1.5 K, which transforms into a sine-modulated magnetic structure at 3.2 and 2.2 K, respectively [7, 8]. Recently, in the search of large MCE and MR, we have studied HoNiSi of this series [9]. In this study, we investigate and compare the properties of the ternary intermetallics of the HoNi*Z* series for *Z* = Ga, Si and Al.

2. Crystal structure and computational details

Both HoNiGa and HoNiSi intermetallic compounds have orthorhombic TiNiSi type crystal structure with *Pnma* space group (62 number) with the lattice parameters: a = 6.811(8) Å, b = 4.274(5) Å and c = 7.318(8) Å [10] for HoNiGa; a = 6.84(3) Å, b = 4.17(2) Å and c = 7.21(3) Å [9] for HoNiSi. For HoNiAl, a = 6.9896(14) Å, b = 6.9896(14) Å and c = 3.8261(4) Å [11], because it is crystallized in the orthorhombic ZrNiAl type crystal structure with *P-62m* space group (189 number). The atomic coordinates are given in table 1. As one can see from figures 1 and 2, the crystal structure for HoNiGa (and HoNiSi) is different from that of HoNiAl which is composed of hexagon motifs in its layers.

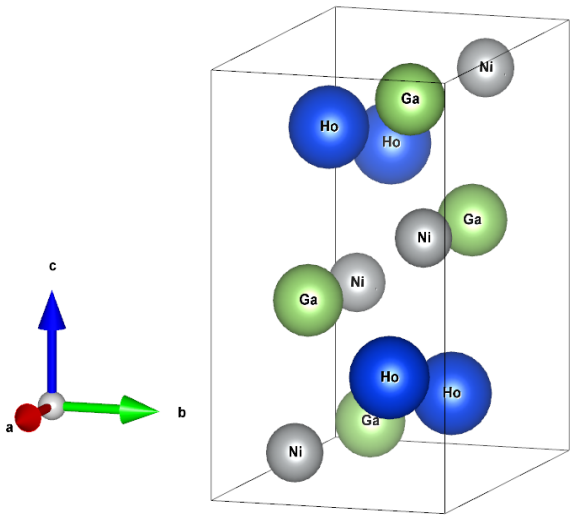

Figure 1. Crystal structure of HoNiGa. The figure was drawn using VESTA software [12].

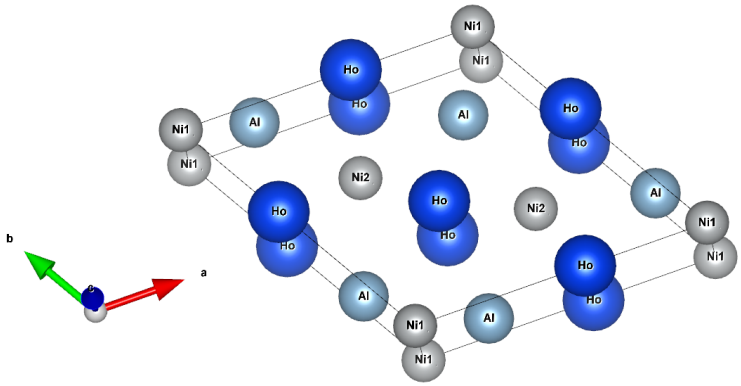

Figure 2. Crystal structure of HoNiAl. The figure was drawn using VESTA software [12].

To study the magnetic properties and electronic structure of the HoNiZ intermetallics, the LSDA+U method was used [13]. It combines local spin density approximation and U correction in the TB-LMTO-ASA package [14]. A linear muffin-tin (MT) orbitals basis used in this package together with atomic sphere approximation included 6s, 6p, 5d and 4f states for Ho; 4s, 4p and 3d states for Ni. The MT radius for Ho was 3.7 a.u., for nickel and silicon - 2.7 and 2.4 a.u., respectively. In the LSDA+U method electronic correlations were taken into account for the 4f shell of the rare-earth ions for the following values of direct Coulomb interaction U = 6.5 eV and exchange J = 0.7 eV parameters [15,16]. The antiferromagnetic ordering of the magnetic moments of the holmium ions was obtained in all three compounds in a good agreement with the experimental data [9-11,17].

Table 1. Atomic coordinates in the compounds HoNiGa, HoNiSi and HoNiAl [9, 10, 11].

Compound	*Site (point symmetry)*	*Coordinates*
HoNiGa	Ho (4c)	0.023; 1/4; 0.695
	Ni (4c)	0.19; 1/4; 0.073
	Ga (4c)	0.298; 1/4; 0.411
HoNiSi	Ho (4c)	0.0212; 1/4; 0.6803
	Ni (4c)	0.142; 1/4; 0.0609
	Si (4c)	0.2651; 1/4; 0.3771
HoNiAl	No (3g)	0.5824(3); 0; 1/2
	Ni1 (1b)	0; 0; 1/2
	Ni2 (2c)	1/3; 2/3; 0
	Al (3f)	0.283(1); 0; 0

3. Results and discussion

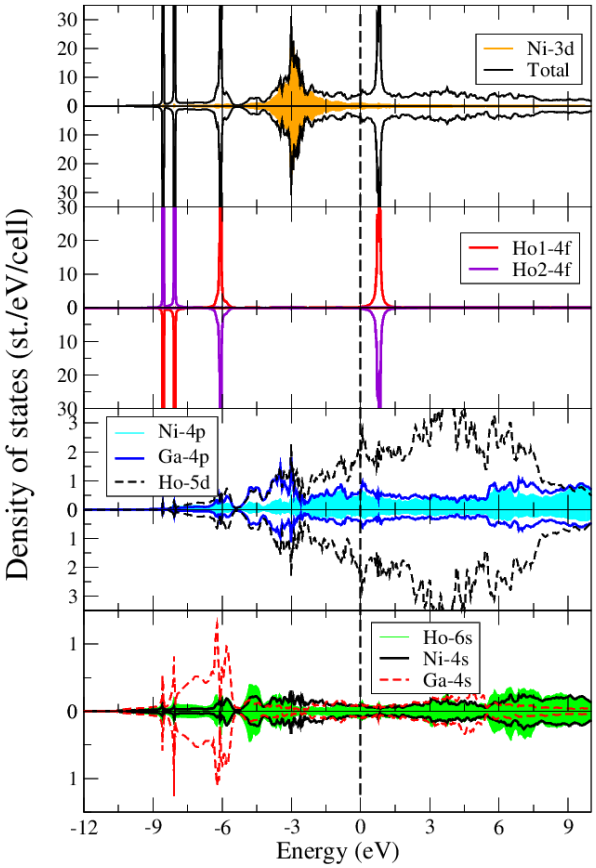

Figure 3. Total and partial densities of electronic states of HoNiGa obtained in our calculations.

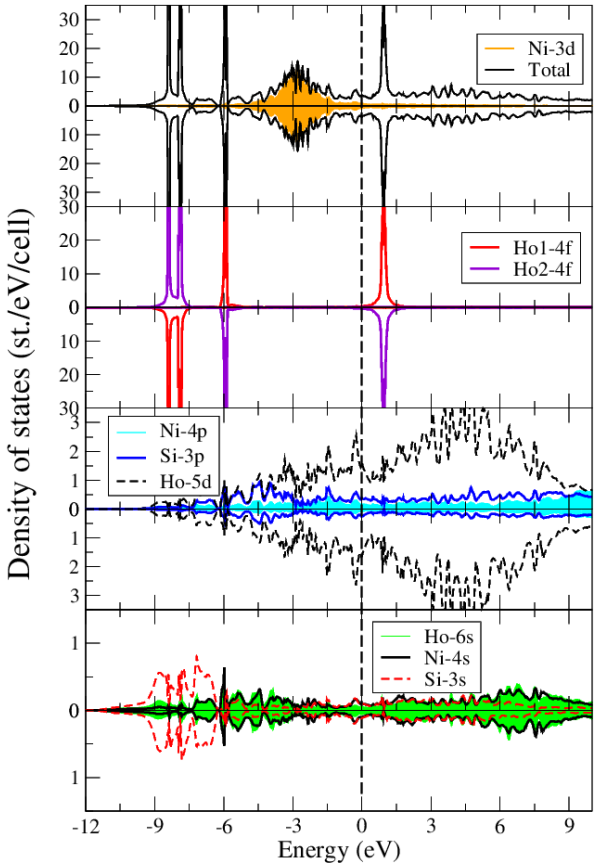

Figure 4. Total and partial densities of electronic states of HoNiSi obtained in our calculations.

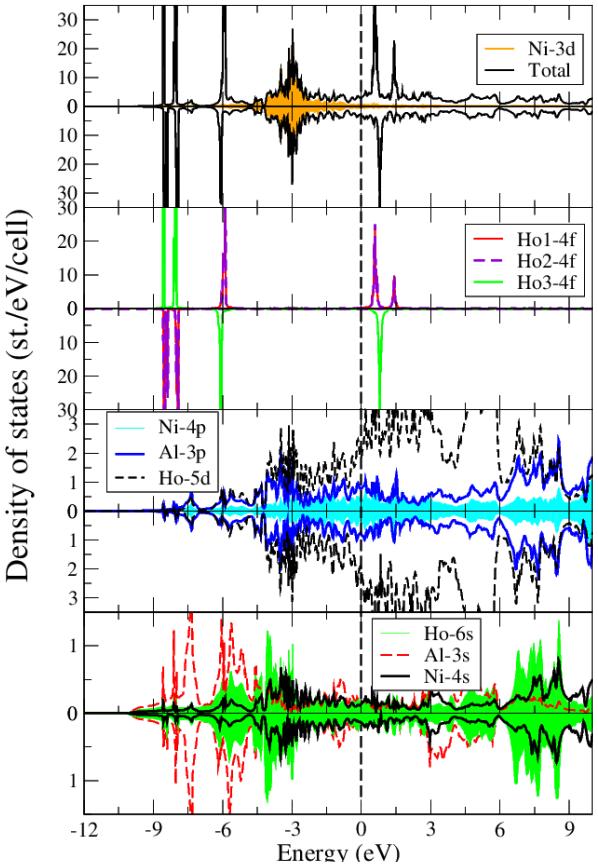

Figure 5. Total and partial densities of electronic states of HoNiAl obtained in our calculations. The Fermi level is located at zero energy.

In figures 3, 4, and 5, the total and partial densities of electronic states of the HoNi*Z* intermetallic compounds (*Z* = Ga, Si, Al) are given for two opposite spin directions up and down, respectively. The Fermi level is located at zero energy. Intense peaks in the total density of states in the HoNiGa compound in figure 3 are formed by the states at energies from -9 to -7.5 eV, then a peak between -6.5 eV and -6.0 eV. These narrow peaks of the density of states are formed due to the 4*f* states of Ho. A wide band in the energy range from -4.5 eV to -0.5 eV is formed by the 3*d* Ni electronic states.

The densities of states in the HoNiSi compound for two opposite spin directions in figure 4 (up and down) are similar to the densities of states of HoNiGa. The intense peaks in the total density of states in the HoNiGa compound in the energy range from -9 to -7.5 eV is broadened due to the 3*s* states of Si. And for the Ga states in the energy range from -4.5 to -0.5 eV, the peaks of the total density of states in this interval are more intense in the HoNiGa compound.

The densities of states of the HoNiAl compound in figure 5 for two opposite spin directions differ from the densities of states of HoNiGa and HoNiSi. The main difference is the presence of three Ho atoms in the HoNiAl compound, and a new peak in the density of states appears at 1.5 eV. The shape of the other electronic states of the *p* elements is also different.

4. Conclusions

Thus, the electronic structure and magnetic ordering of the ternary intermetallics of the HoNi*Z* series (*Z* = Ga, Si, Al) were calculated using the LSDA+*U* method. The antiferromagnetic ordering of the Ho magnetic moments was obtained in all three ternary compounds. An analysis of the densities of

electronic states in the HoNiGa, HoNiSi, and HoNiAl compounds obtained accounting for electronic correlations revealed that the main difference comes from the presence of different number of the Ho ions in HoNiAl and other two ternary intermetallics, as well as the different *p* element in all three compounds.

Acknowledgments
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